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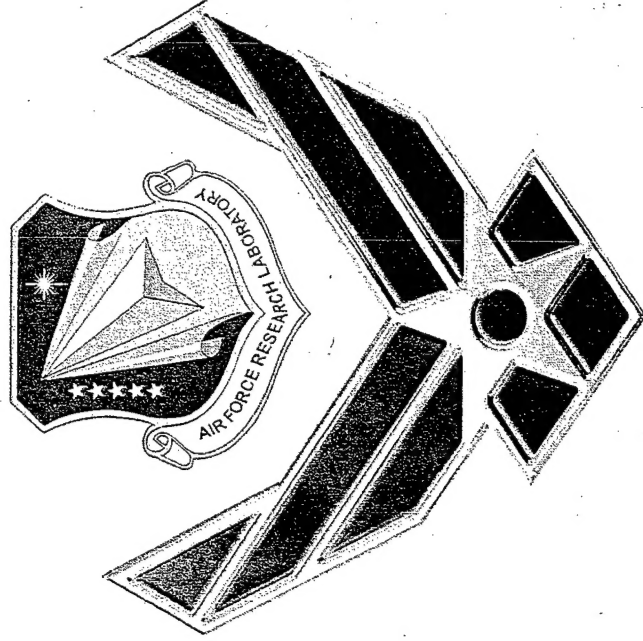
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# **Update in Ionic** **Liquids Research**



**Greg Drake and Tommy Hawkins**

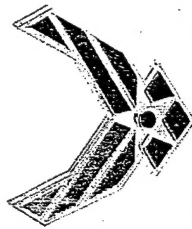
**AFRL/PRSP**

**AFOSR Ionic Liquids Workshop**

**March 7 & 8, 2004**

**Tampa, FL**

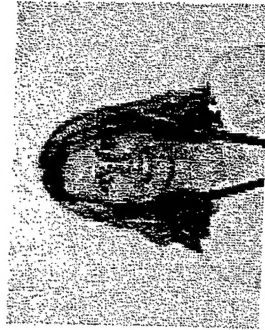
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# AFRL Ionic Liquids



## Those involved in this work



Ms. Kerri Tollison  
Synthesis and  
Characterization



Greg Kaplan  
Synthesis and  
Characterization



Jerry Boatz  
Theoretical  
Calculations



Jeff Mills  
Theoretical  
Calculations



Leslie Hall  
Synthesis &  
x-ray work



Ashwani Vij  
X-ray  
crystallography



Tommy Hawkins  
6.2 Propellant  
Development

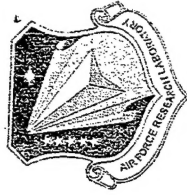


Greg Drake  
6.1 Research  
Synthesis

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# AFRL Ionic Liquids



## HOW WE GOT TO WHERE WE ARE

- SIMPLE SALTS USING PROTIC ACIDS

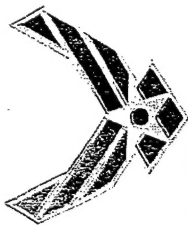
- OPEN CHAIN WORK  
HYDROGEN BONDING EFFECTS

HYDRAZINE ANALOGUES

SOME SIMPLE AMINES

- HETEROCYCLIC APPROACH

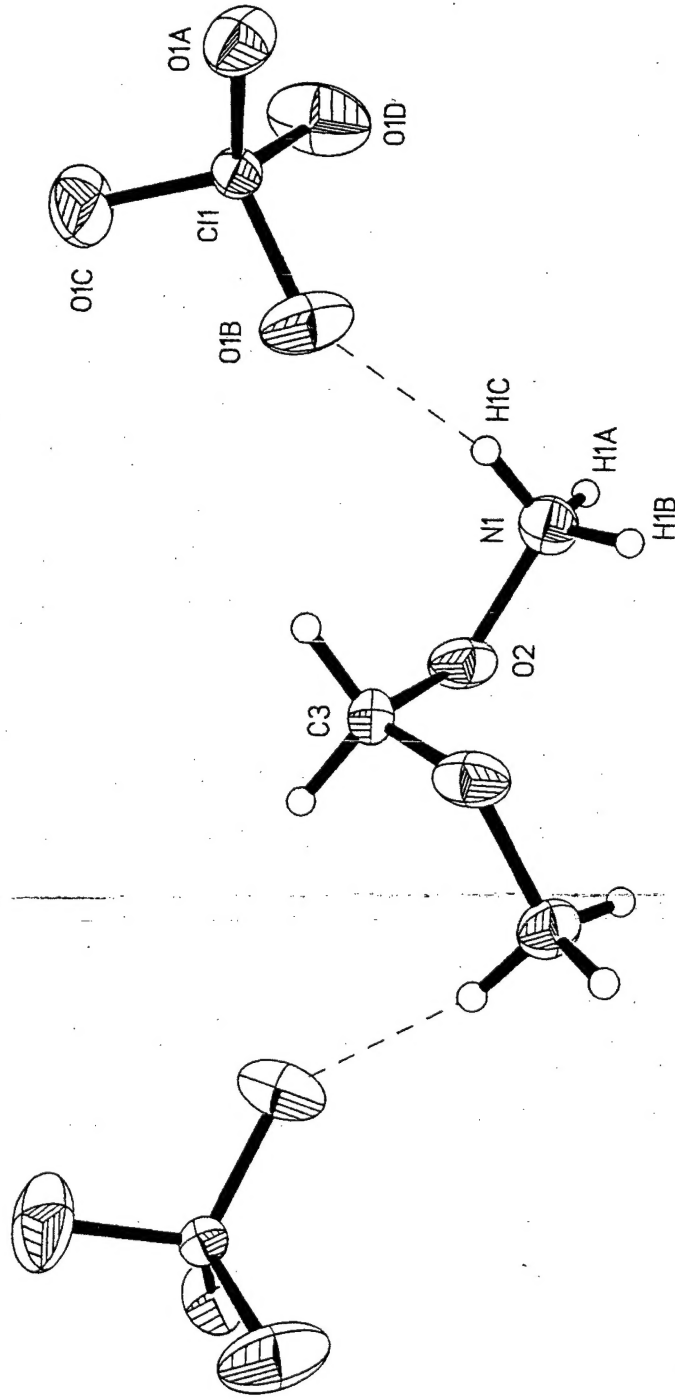
SHAPE CONSIDERATIONS



# AFRL Ionic Liquids

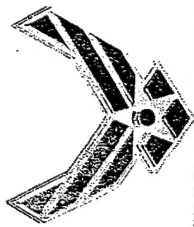


- Oxyamine,  $\text{-O-NH}_2$ , is analogue to hydrazine linkage  $\text{-NH-NH}_2$
- $\text{CH}_2(\text{O-NH}_2)_2$  Explored at Edwards in late 1960's (Claude Merrill)
- Reinvestigation of mono- and di- salts
- Several of the salts met the definition of an ionic liquid
- Treacherous! Sensitive to mechanical stimuli! Explode unexpectedly!

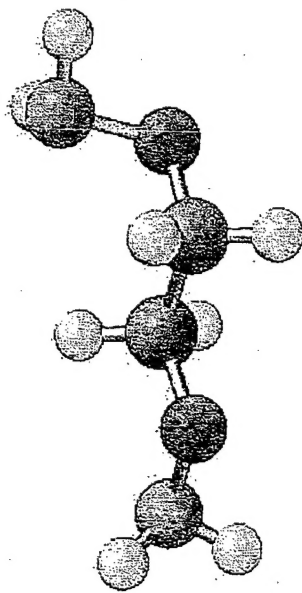
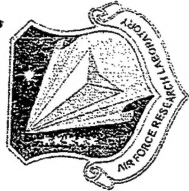


Tollison, K.; Drake, G.; Hawkins, T.; Brand, A.; McKay, M.; Ismail, I.; Merrill, C.; Petrie, M.; Bottaro, J.; Highsmith, T.; Gilardi, R. J. Energet. Mater. 2001, 19, 277.

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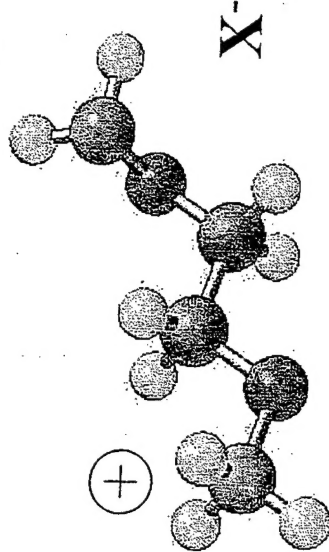
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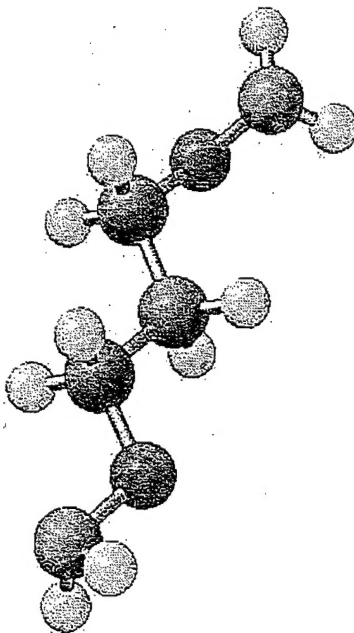
1,2-bis(oxyamine)ethane

Dixon, D. W.; Weiss, R. H. J Org. Chem. 1984,49, 4487.

H-X

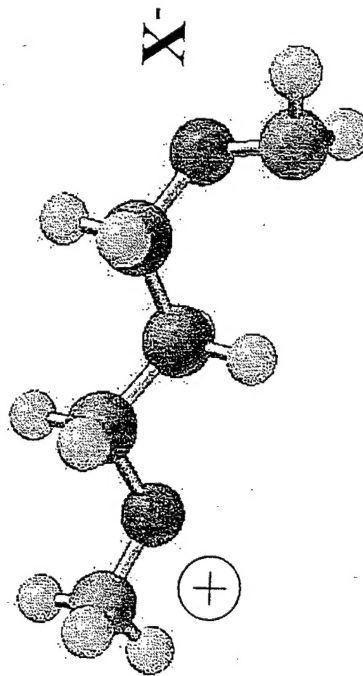


1,2-bis(oxyamine)ethane mono salts  
 $X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$



1,3-bis(oxyamine)propane very stable, watery liquid  
b.p. = 65-70 C @ 0.3 torr; f.p. = glasses at -40 C

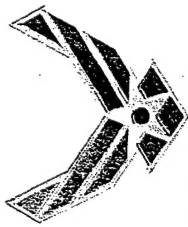
H-X



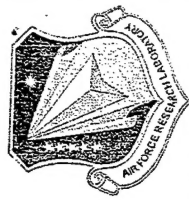
1,3-bis(oxyamine)propane mono salts  
 $X^- = NO_3^-, ClO_4^-, C(NO_2)_3^-, N(NO_2)_2^-$

In either case, the oxyamines yield extremely friction and impact sensitive materials.

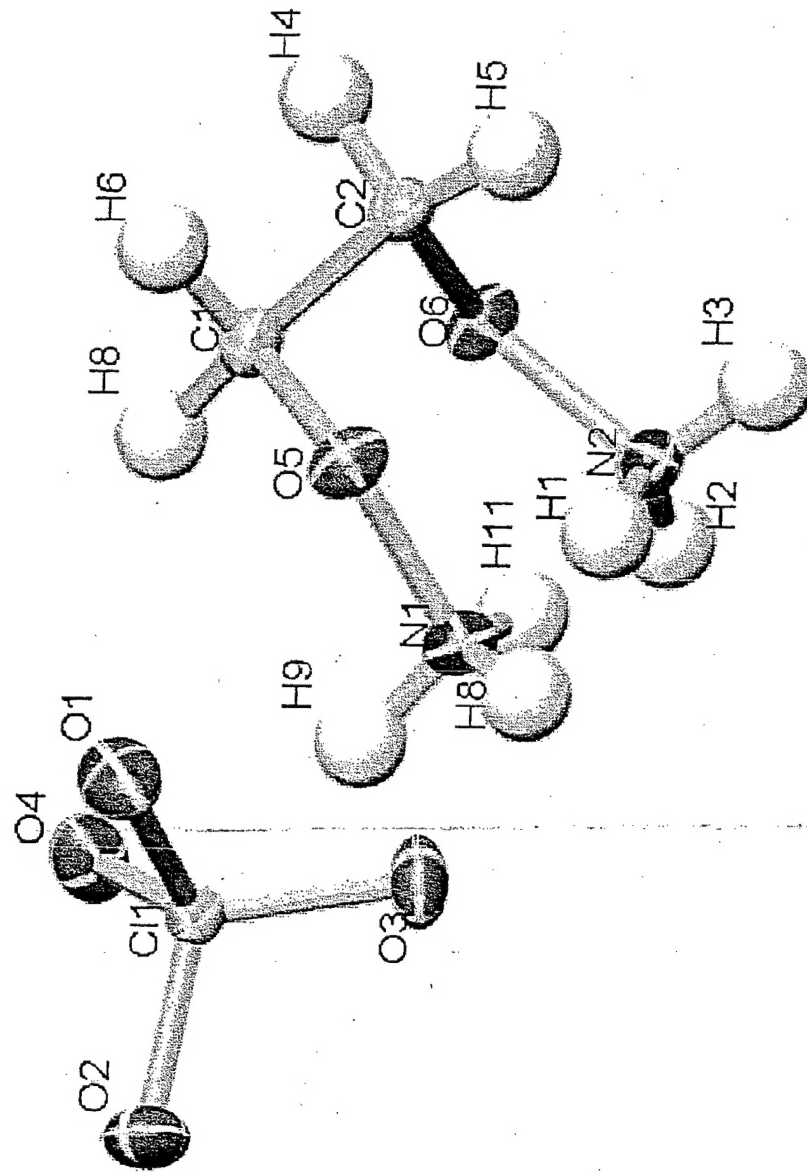
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.  
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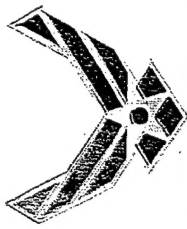


X-ray diffraction confirmed structure, lots of hydrogen bonding!  
H(1) and H(8) are partial occupancy 70%/30%



Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.  
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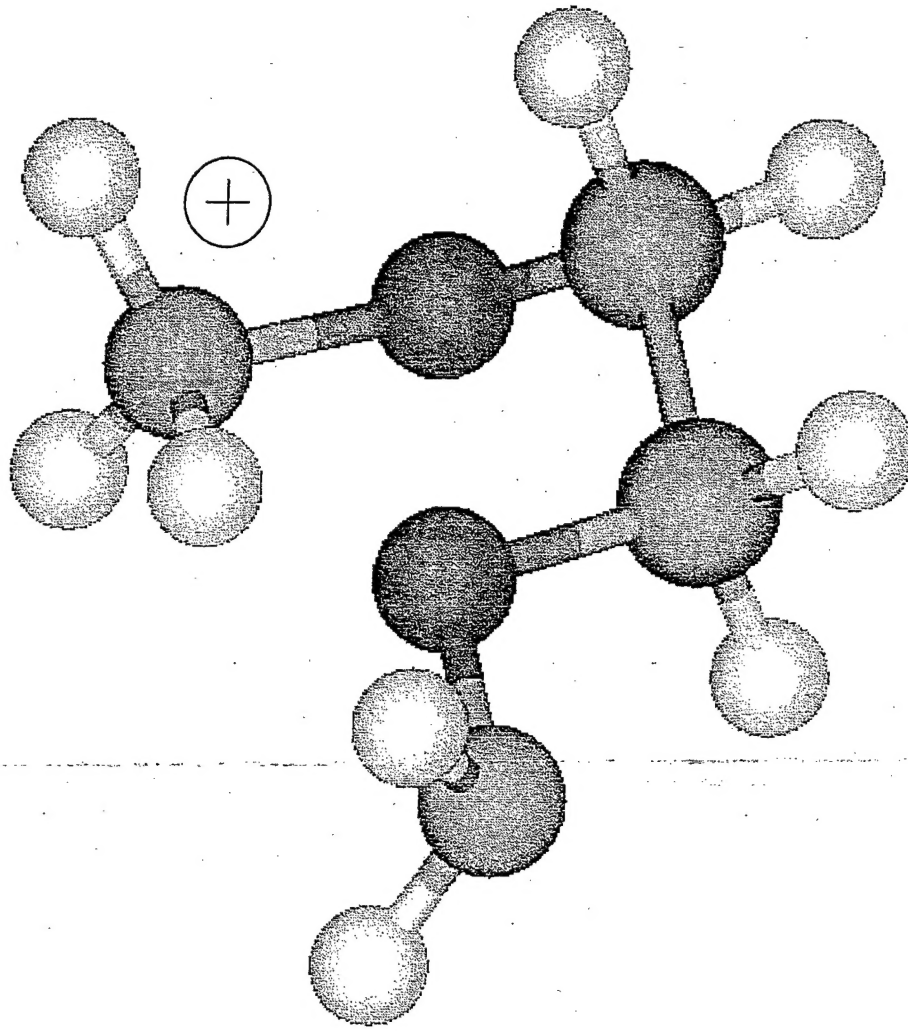




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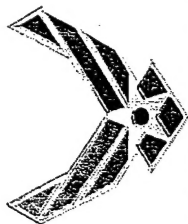


High level computational studies (Dr. Jeff Sheehy NASA/Marshall) revealed a slightly different structure. Comparison of bond distances matched well though

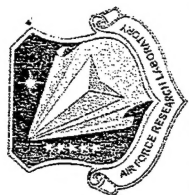


Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted 2004.  
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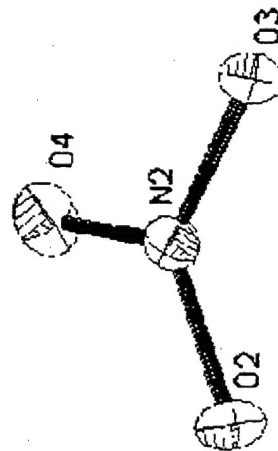
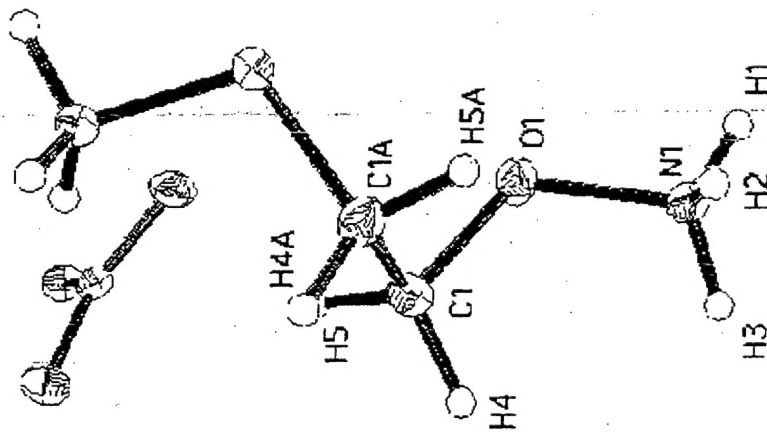




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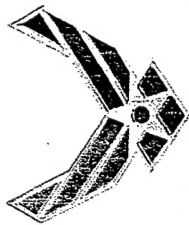


X-ray structure ethylene bisoxayamine dinitrate was also solved

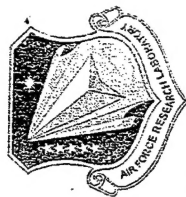


Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. *Prop. Energ. Pyrotech.* Submitted 2004.

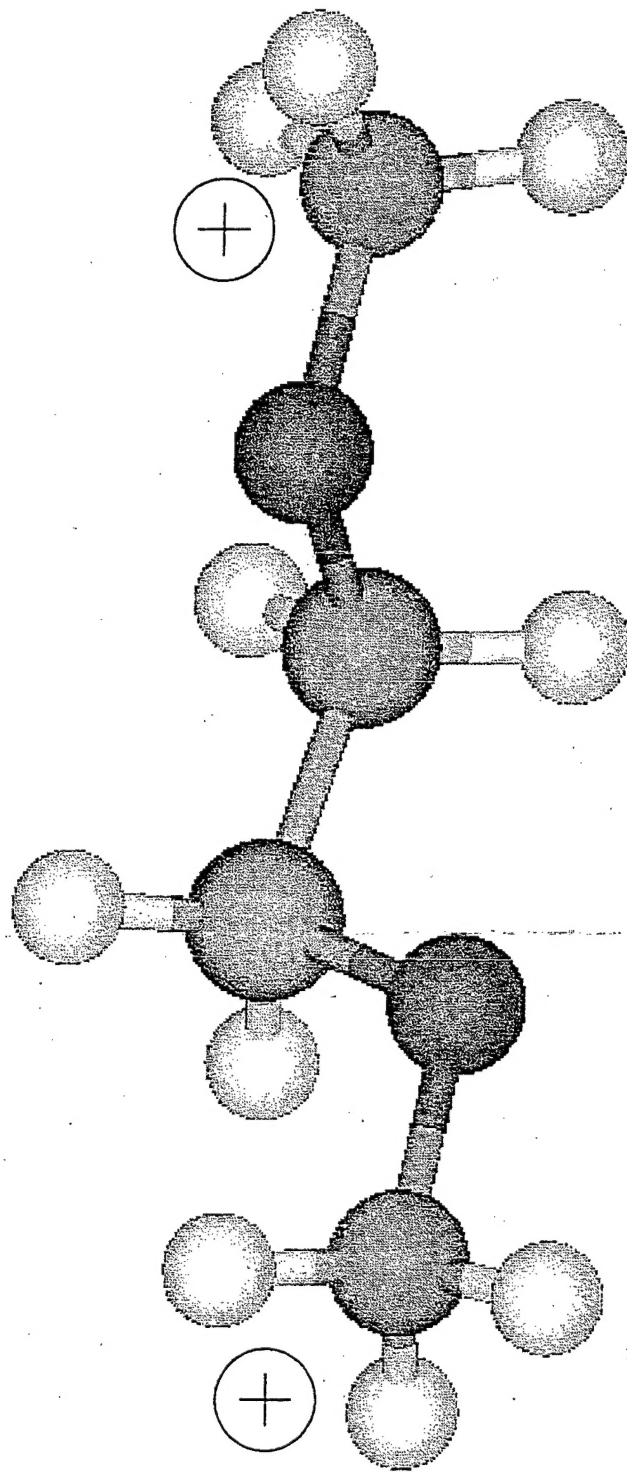
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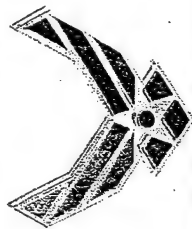
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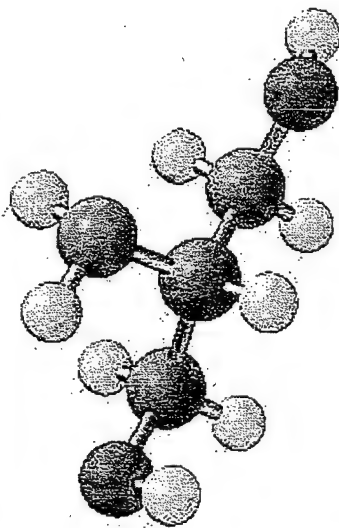
High level calculations (Jeff Sheehy) of the gas phase ethylene bisoxammonium Dication revealed a similar structure with accurately predicted bond distances.



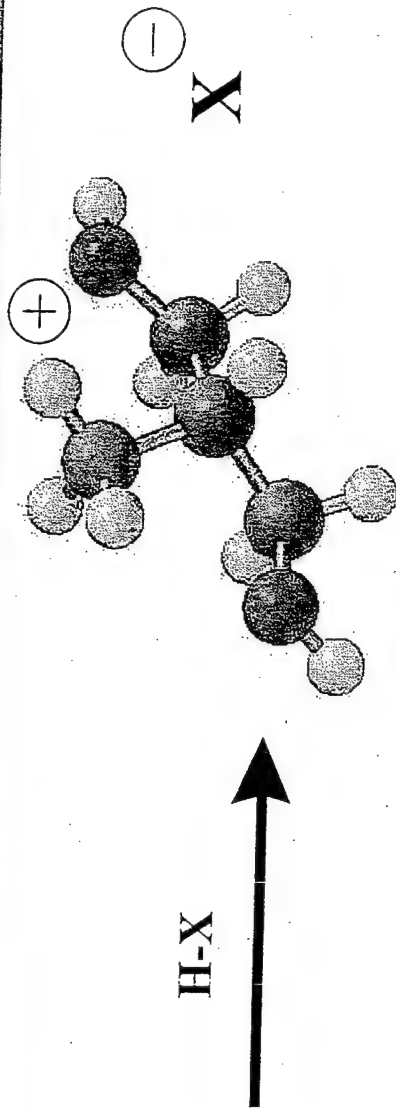
Drake, G.; Hawkins, T.; Hall, L.; Sheehy, J. Prop. Energ. Pyrotech. Submitted **2004**.  
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# AFRL Ionic Liquids



1,3-dihydroxy-2-aminopropane  
(serinol)



Salt	m.p.	DSC onset	Impact (kg-cm)	Friction (kg)
Serinol nitrate	61-66° C	215° C	180	18.0
Serinol perchlorate	55-60° C	250° C	200	>37.8
Serinol dinitramide	41-44° C	135° C	16	23.4

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. Prop. Energ. Pyrotech. 2004 submitted.

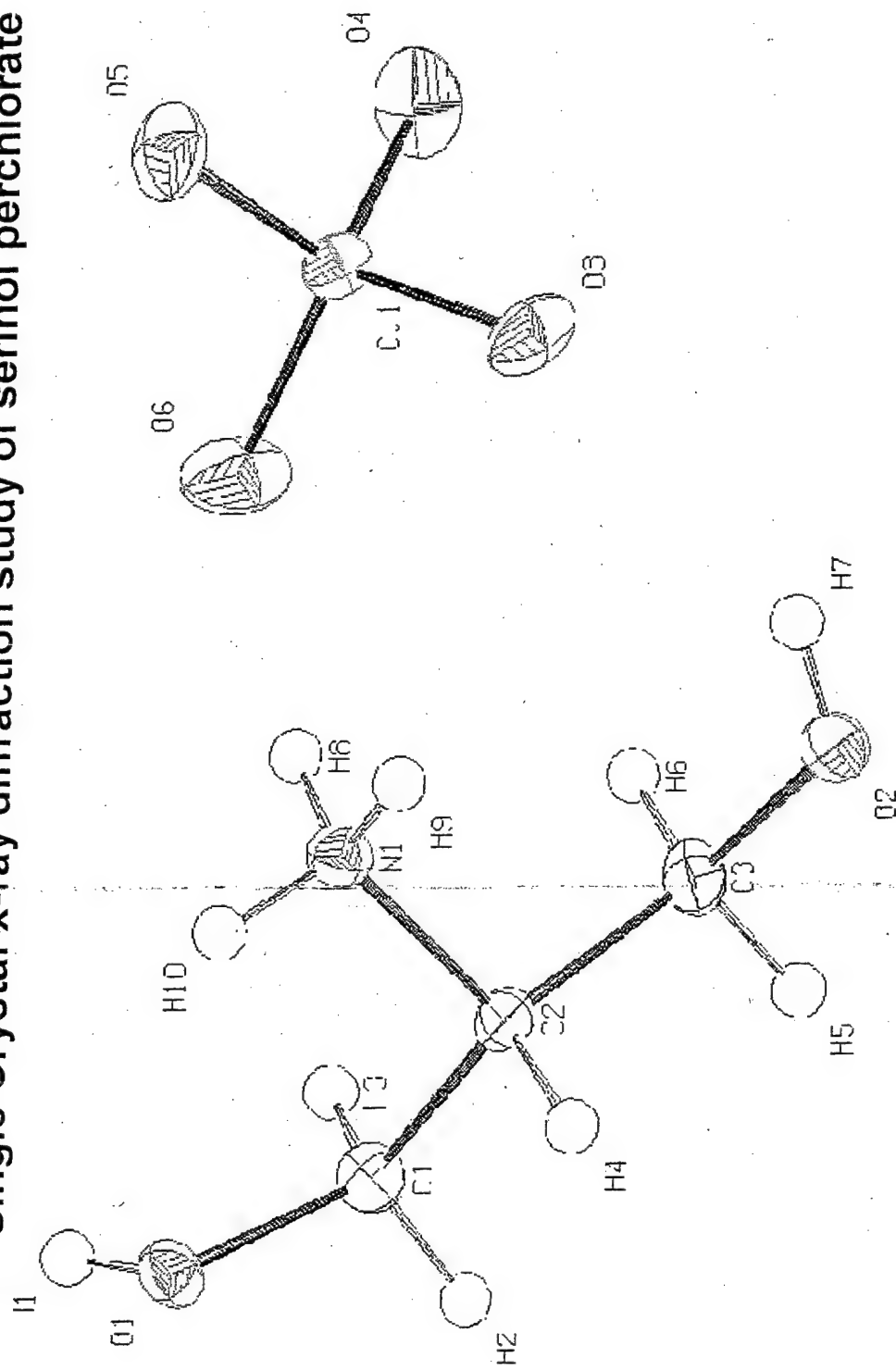
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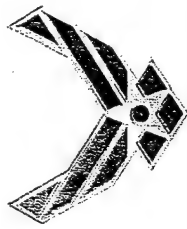


# AFRL Ionic Liquids

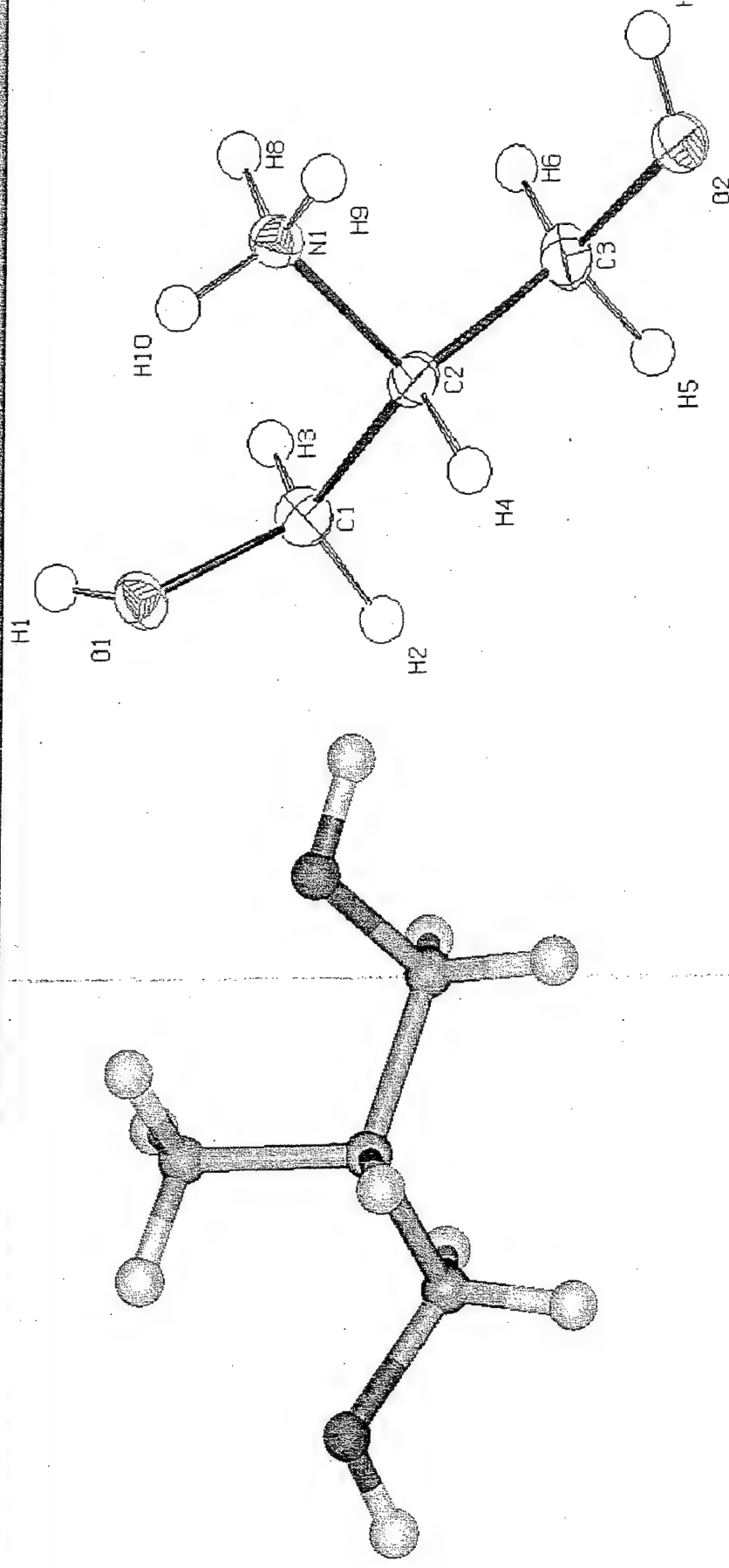


## Single Crystal x-ray diffraction study of serinol perchlorate

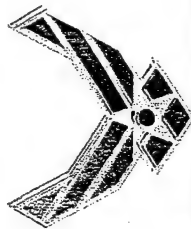




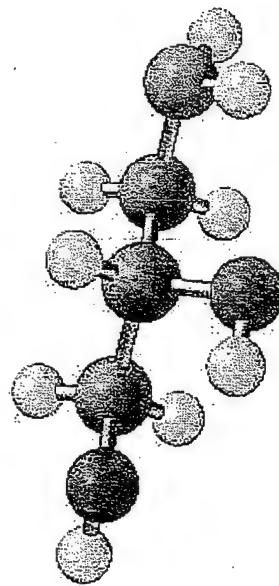
# AFRL Ionic Liquids



Theoretical computations by Dr. Jerry Boatz (AFRL) using B3LYP/6-31G(d,p) of serinol cation in the gas phase ( $C_s$  symmetry) as compared to that observed in the single crystal x-ray diffraction study of serinol perchlorate

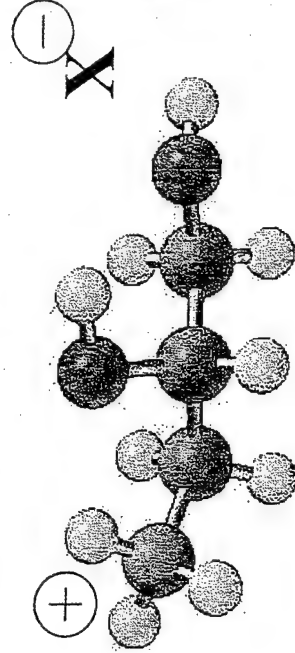


# AFRL Ionic Liquids



1,2-dihydroxy-3-aminopropane  
(chiral)

H-X



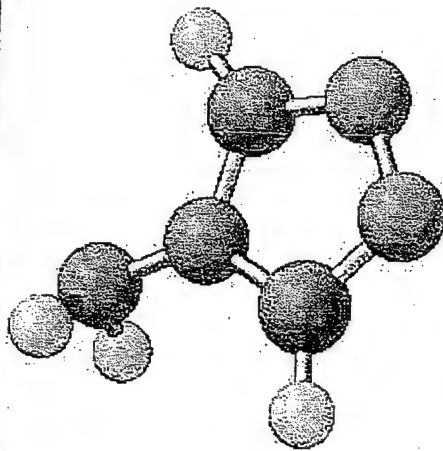
$X^- = \text{NO}_3^-, \text{ClO}_4^-, \text{N}(\text{NO}_2)_2^-$

<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>
1,2-dihydroxy-3-aminopropane nitrate	-40° C	220° C
1,2-dihydroxy-3-aminopropane perchlorate	?	225° C
1,2-dihydroxy-3-aminopropane dinitramide	-5° C	135° C

Drake, G.; Hawkins, T.; Tollison, K.; Hall, L.; Boatz, J. manuscript in progress, 2004.  
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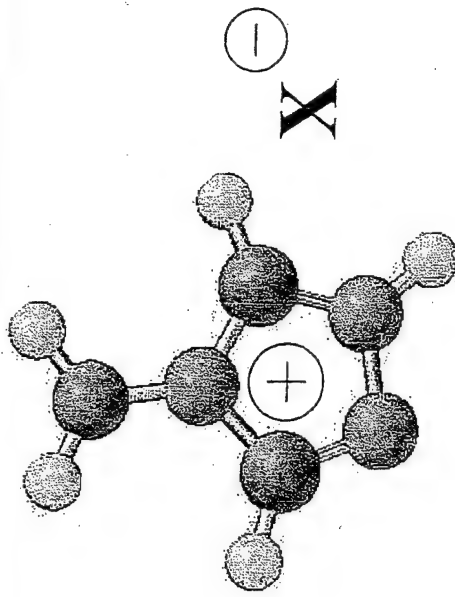


# AFRL Ionic Liquids



4-amino-1,2,4-triazole

H-X



<u>SALT</u>	<u>Melting Point</u>	<u>Decomposition Onset</u>	<u>Impact</u> kgcm
4-amino-1,2,4-triazolium nitrate	69° C	180° C	>200
4-amino-1,2,4-triazolium perchlorate	84° C	210° C	30
4-amino-1,2,4-triazolium dinitramide	20° C	145° C	<5

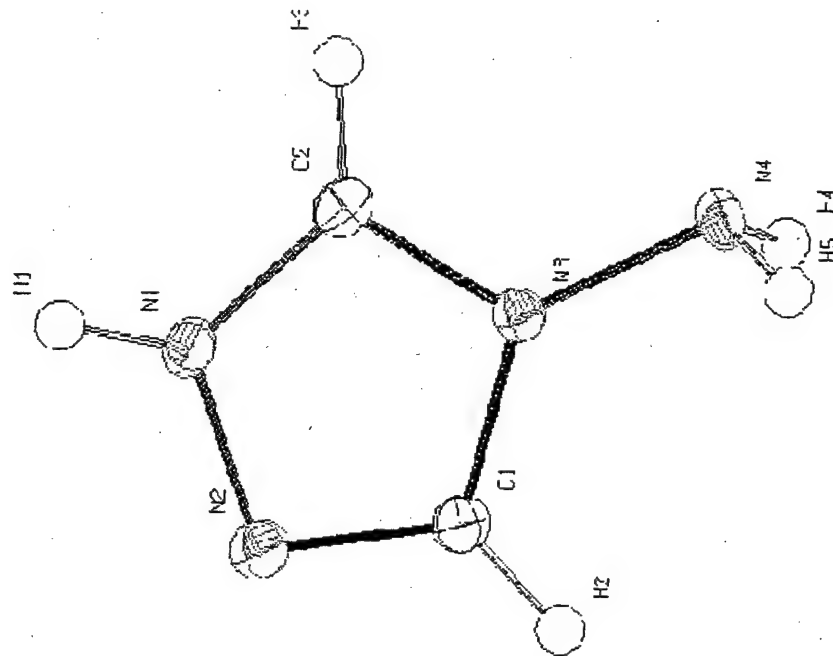
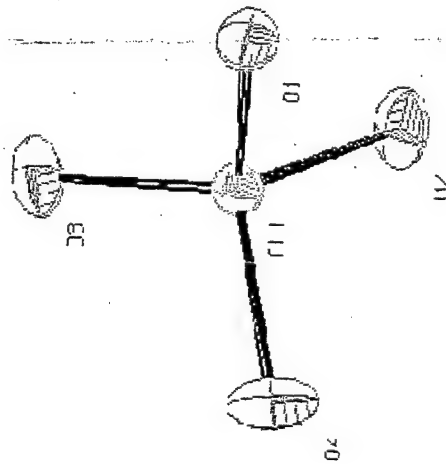




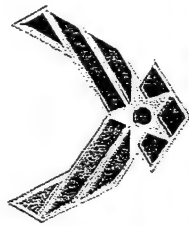
# AFRL Ionic Liquids



Single crystal x-ray diffraction study revealed the expected structure for 4-amino-1,2,4-triazolium perchlorate.



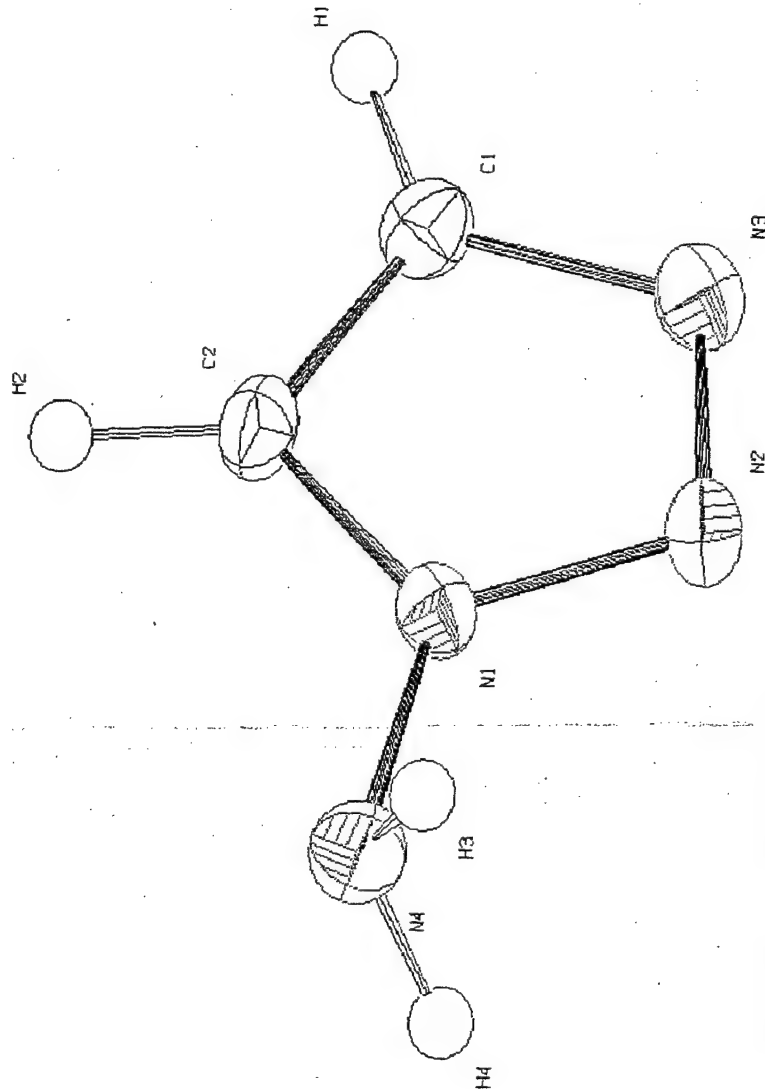
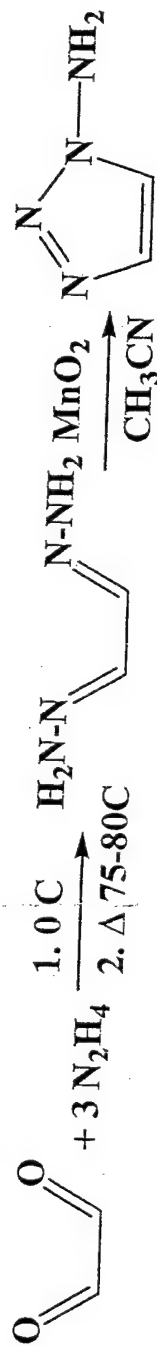
Hall, L.; Drake, G. Unpublished results 2004.  
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# AFRL Ionic Liquids



## New Effort with 1-amino-1,2,3-triazole



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.

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# AFRL Ionic Liquids



## Synthesis of 1-amino-3-alkyl-1,2,3-triazolium halides



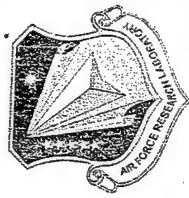
New Salt	M.P. (°C)	Decomp.
1-amino-3-methyl-1,2,3-triazolium iodide	146	150
1-amino-3-ethyl-1,2,3-triazolium bromide	118	149
1-amino-3-propyl-1,2,3-triazolium bromide	128	135
1-amino-3-allyl-1,2,3-triazolium bromide	100	135
1-amino-3-butyl-1,2,3-triazolium bromide	131	145

## Not Ionic Liquids!

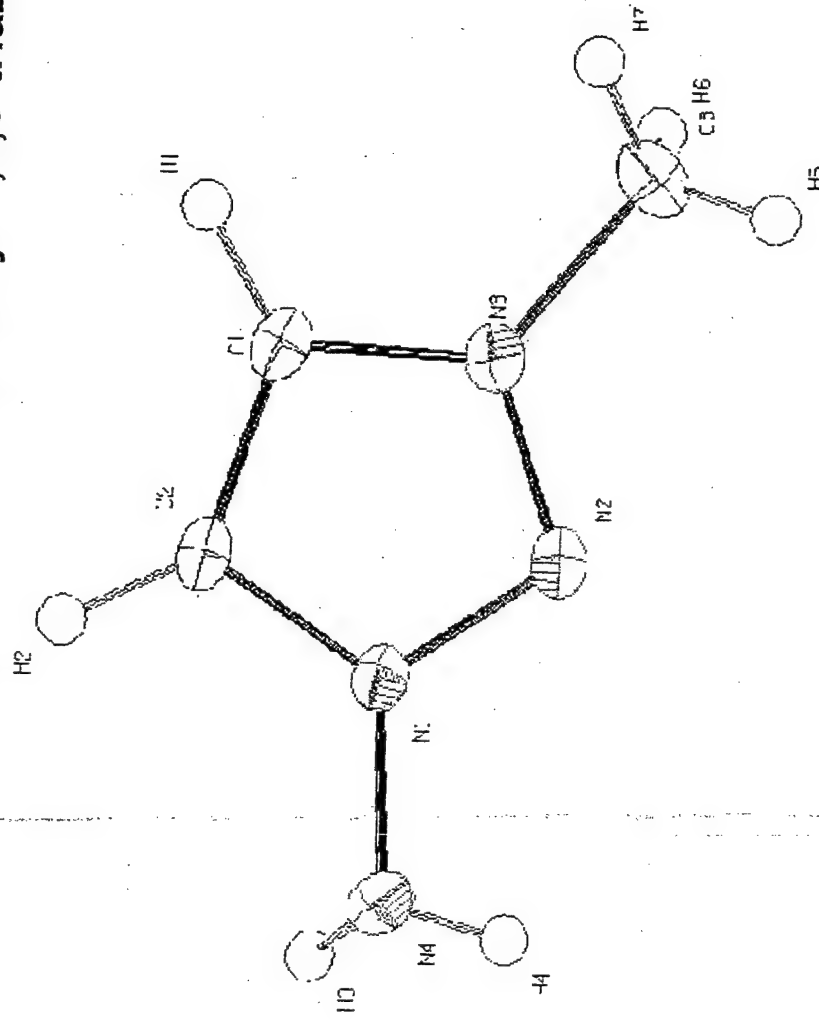
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.  
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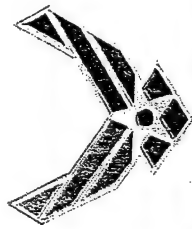


Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium iodide



11

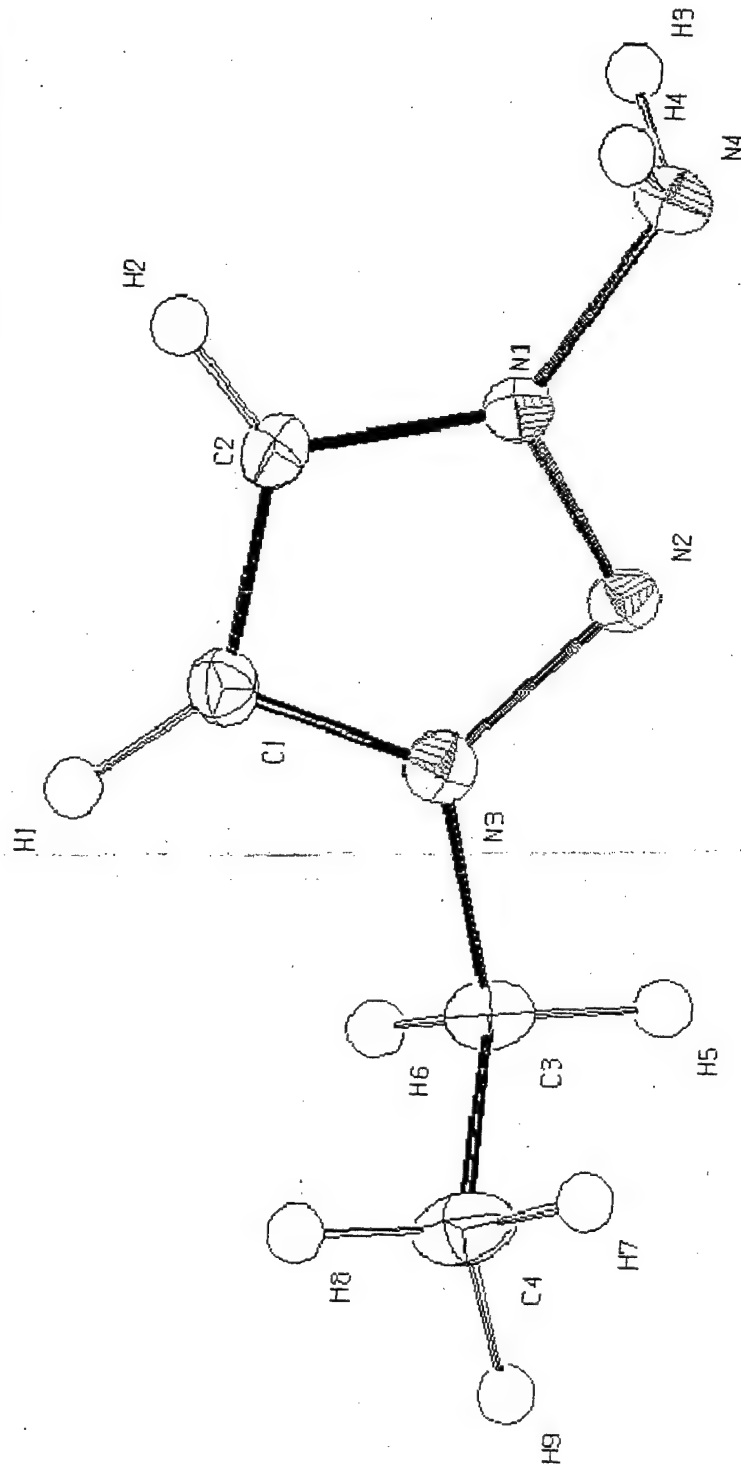
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.  
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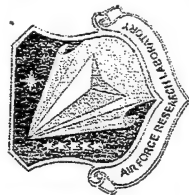
## Single crystal x-ray diffraction study of 1-amino-3-ethyl-1,2,3-triazolium bromide



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.  
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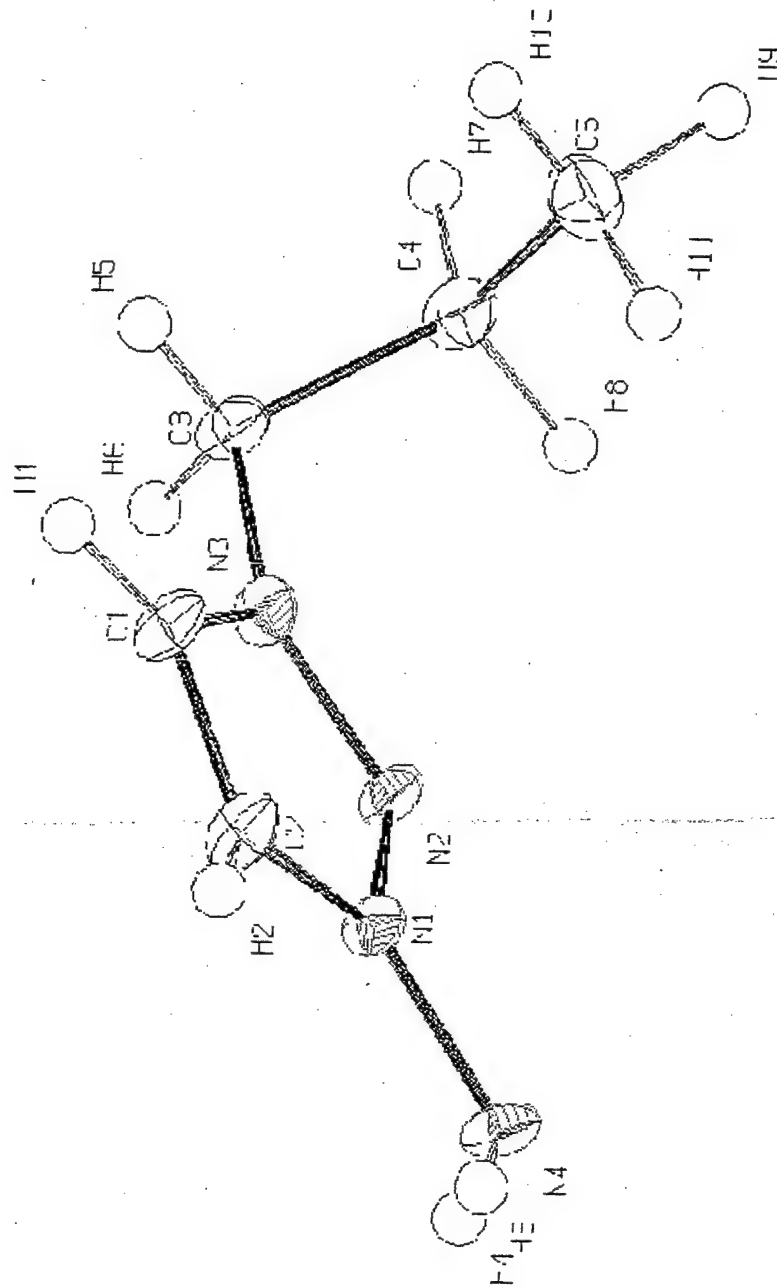


# AFRL Ionic Liquids



## Single crystal x-ray diffraction study of 1-amino-3-propyl-1,2,3-triazolium bromide

Br 1



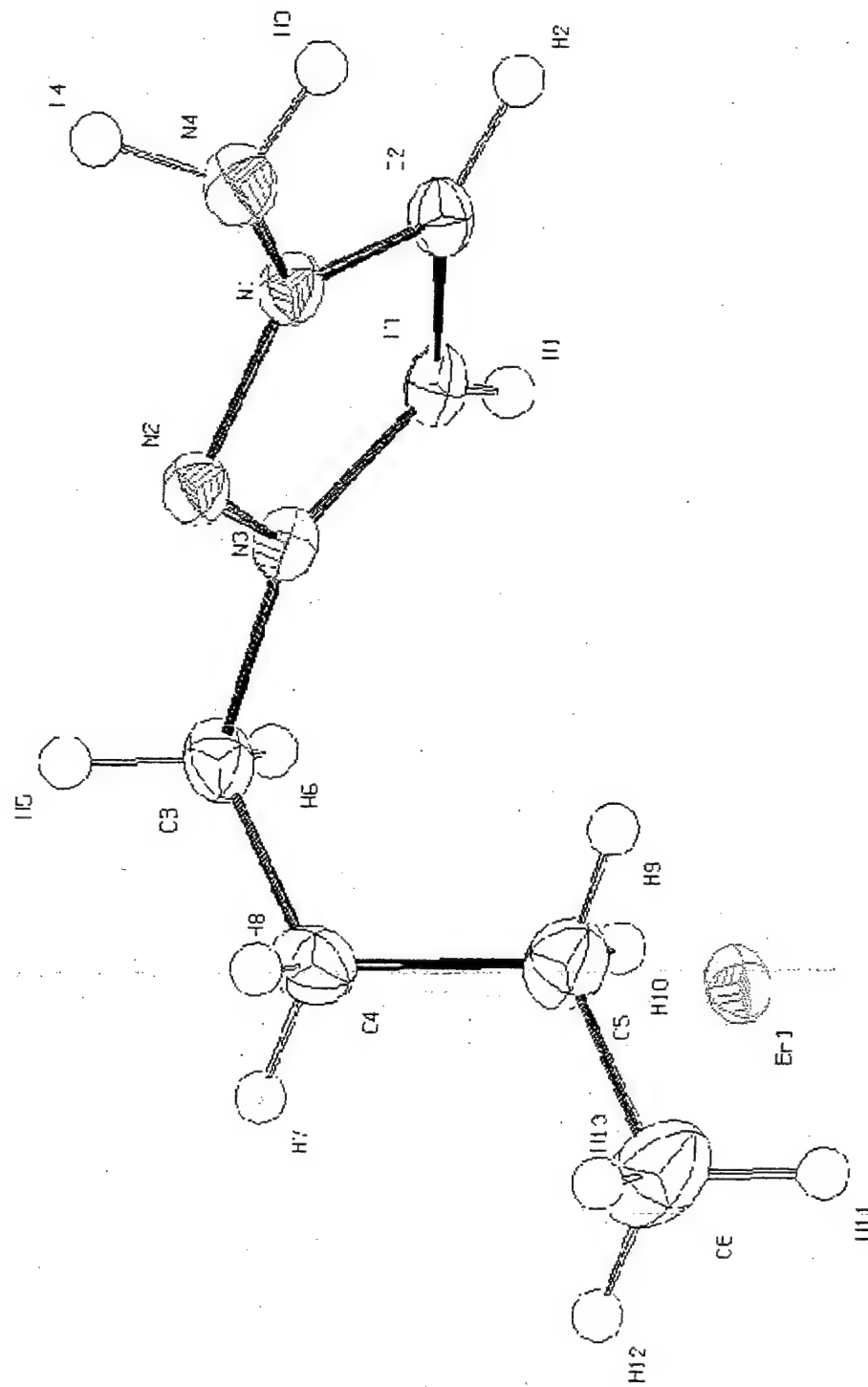
Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.  
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## Single crystal x-ray structure of 1-amino-3-butyl-1,2,3-triazolium bromide



Kaplan, G.; Drake, G.; Hawkins, T.; Tollison, K.; Hall, L. J. *Heterocyc. Chem.* submitted 2004.

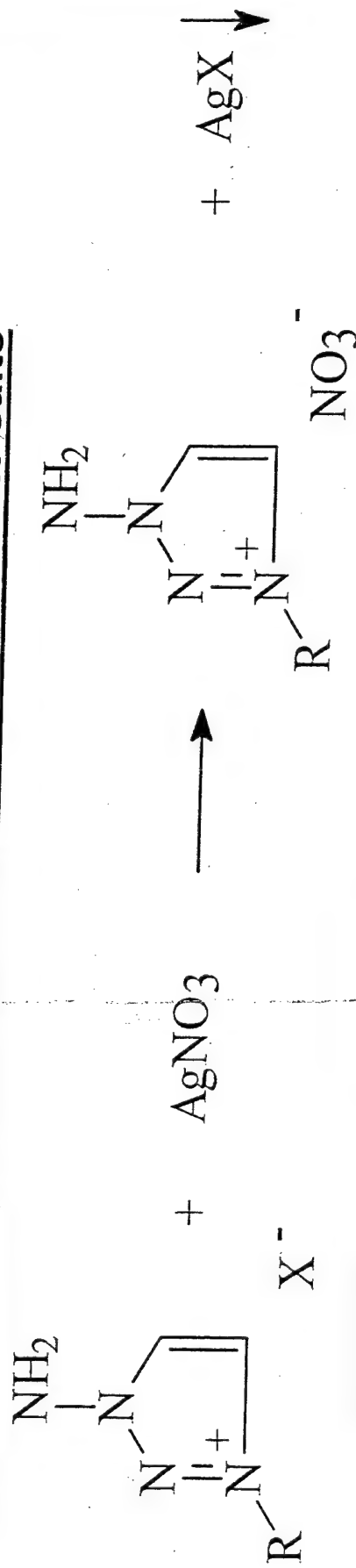
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# AFRL Ionic Liquids

Straight-forward metathesis forms desired nitrate salts



<u>NEW SALT</u>	M.P. (°C)
1-amino-3-methyl-1,2,3-triazolium nitrate	86
1-amino-3-ethyl-1,2,3-triazolium nitrate	30
1-amino-3-propyl-1,2,3-triazolium nitrate	33
1-amino-3-allyl-1,2,3-triazolium nitrate	8
1-amino-3-butyl-1,2,3-triazolium nitrate	48

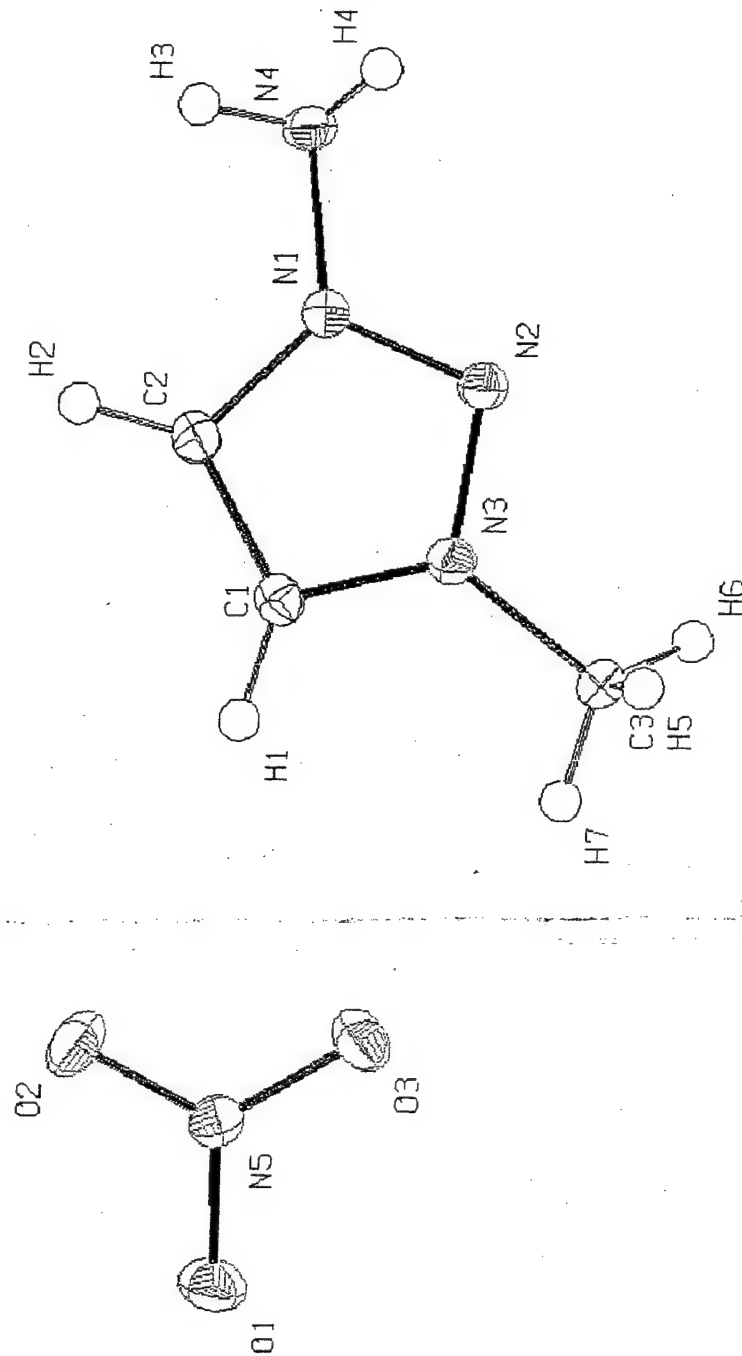
Kaplan, G.; Drake, G.; Tollison, K.; Hawkins, T.; Hall, L. Manuscript in progress 2004.  
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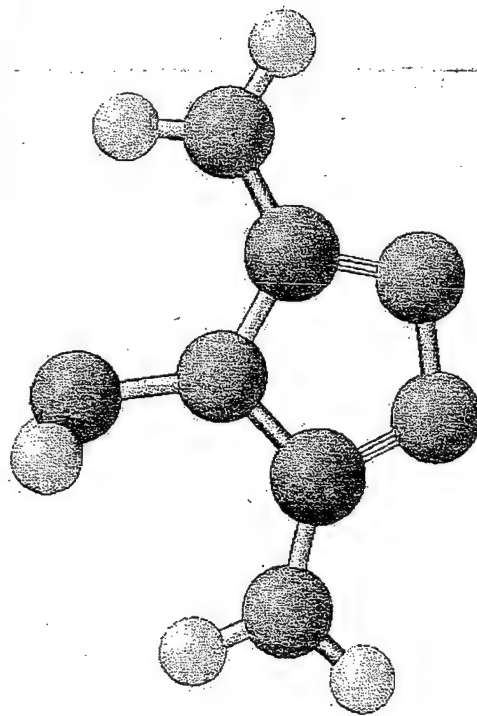
## Single crystal x-ray diffraction study of 1-amino-3-methyl-1,2,3-triazolium nitrate



Kaplan, G.; Drake, G.; Hawkins, T.; Hall, L.; Tollison, K. Manuscript in progress 2004  
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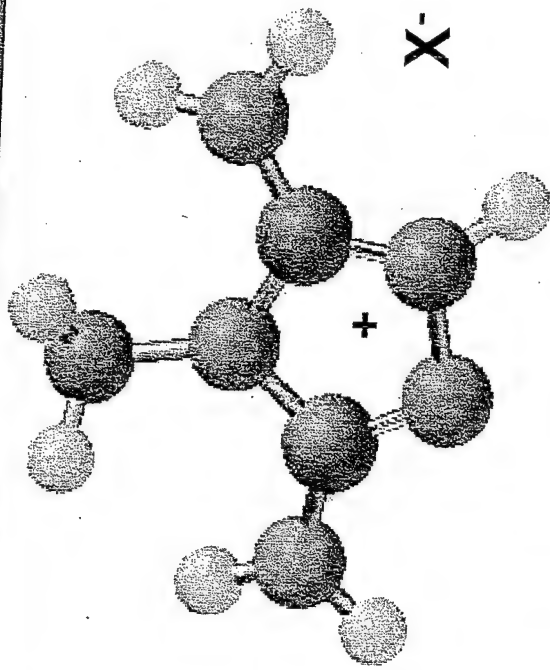


# AFRL Ionic Liquids



3,4,5-triamino-1,2,4-triazole  
(Guanazine)

+ H-X

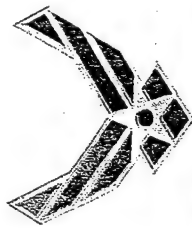


$X^- = NO_3^-, ClO_4^-, N(NO_2)_2^-$

<u>New Salt</u>	M.P. ( $^{\circ}C$ )	Impact (kgcm)	Friction (Kg)
Guanazinium nitrate	225	200	16
Guanazinium perchlorate	215	50	15.2
Guanazinium dinitramide	145	196	15.2

Not Ionic Liquids!

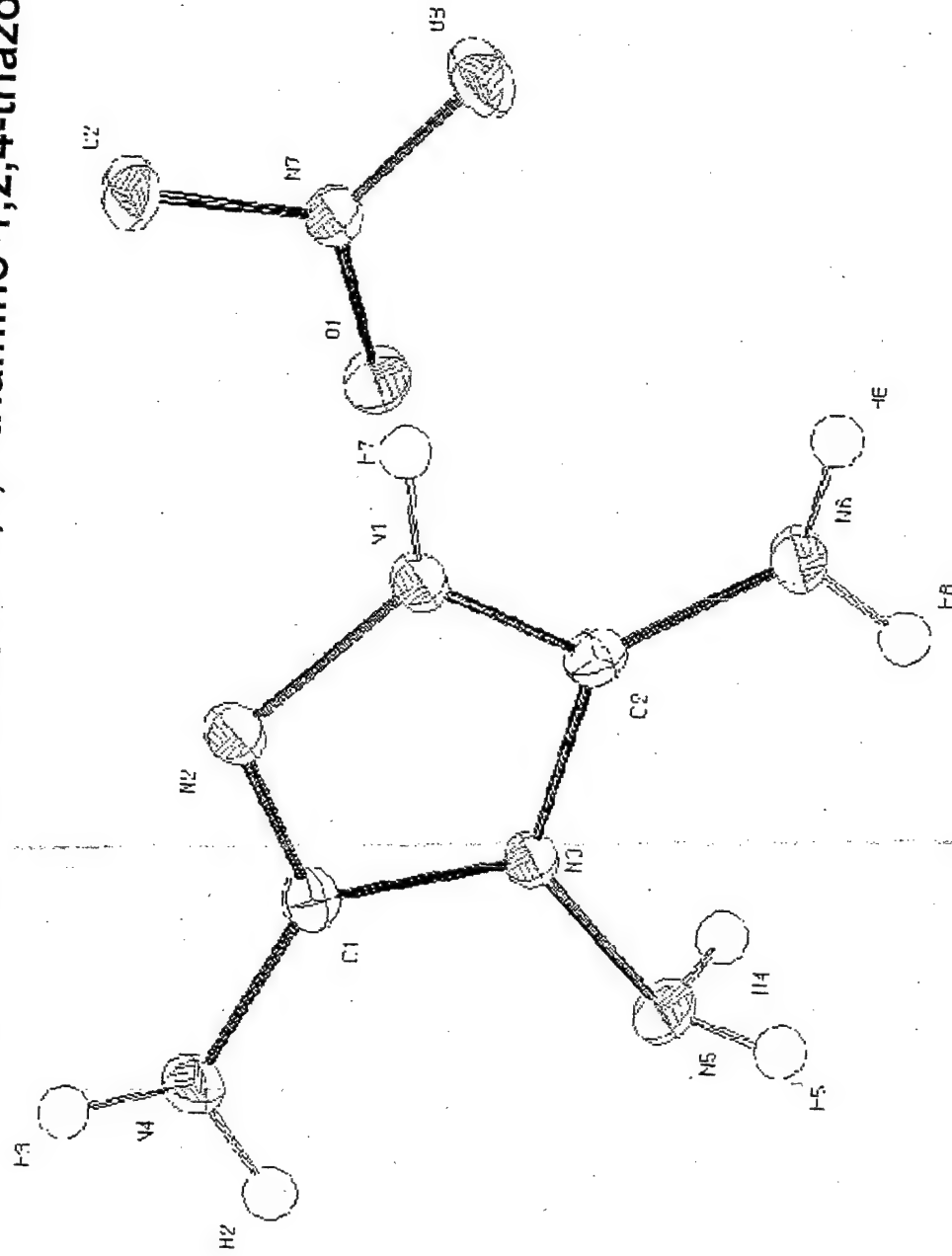
Drake, G.; Hawkins, T.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted  
Distribution A. Public Release, Distribution unlimited



# AFRL Ionic Liquids



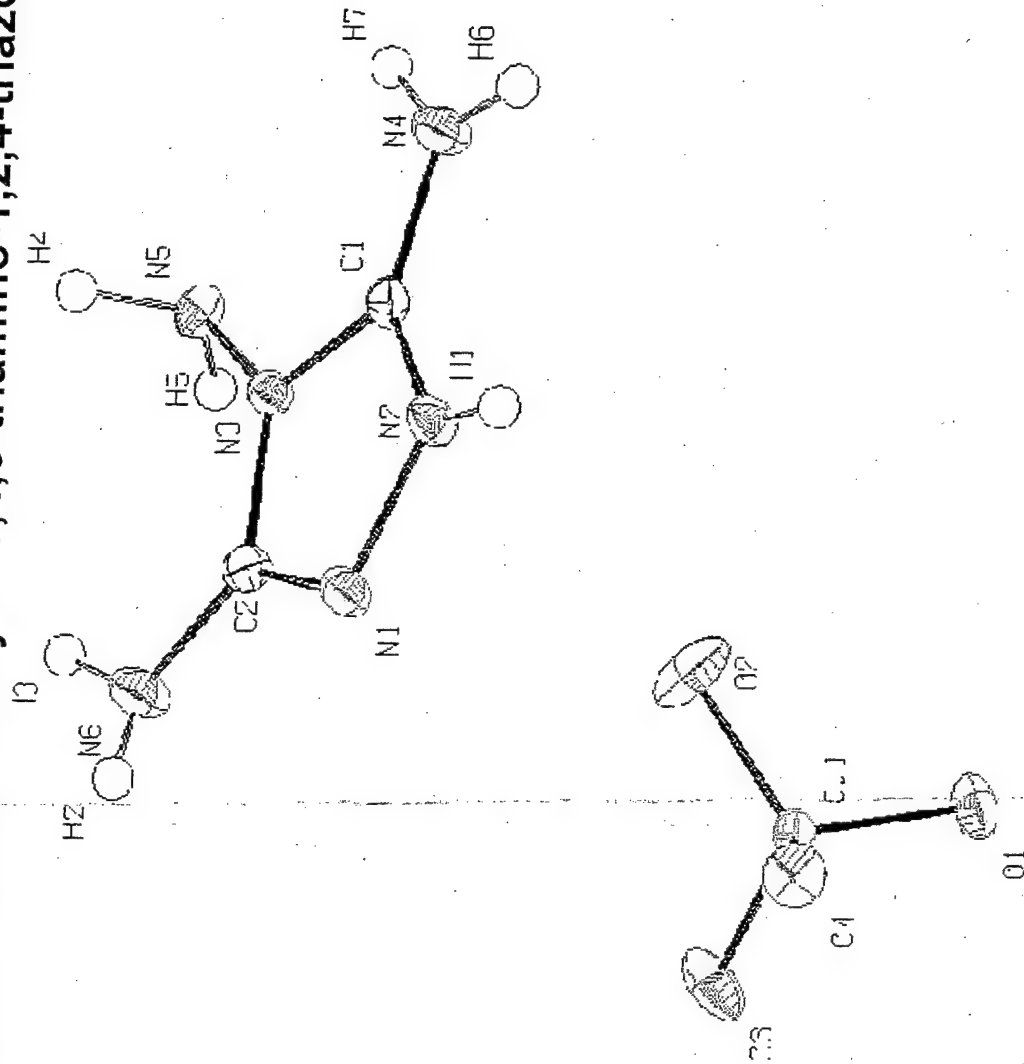
Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium nitrate



Drake, G.; Hawkins, T.; Hall, L.; Brand, A. *Prop. Expl. Pyrotech.* **2004**, to be submitted  
Distribution A. Public Release, Distribution unlimited



# Single crystal x-ray diffraction study of 3,4,5-triamino-1,2,4-triazolium perchlorate



Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted

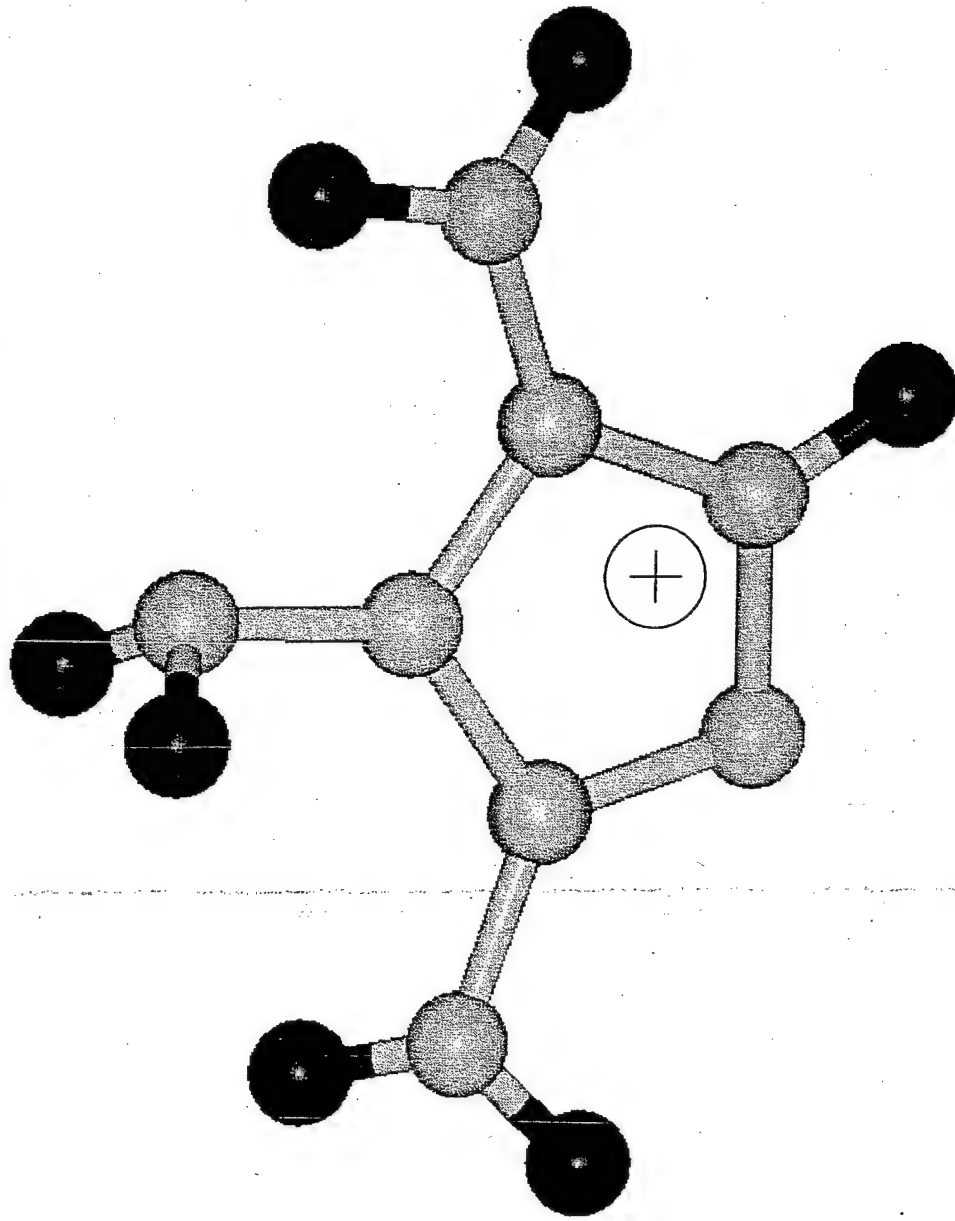
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# AFRL Ionic Liquids



## Theoretical Calculations of protonated 3,4,5-triamino-1,2,4-triazole



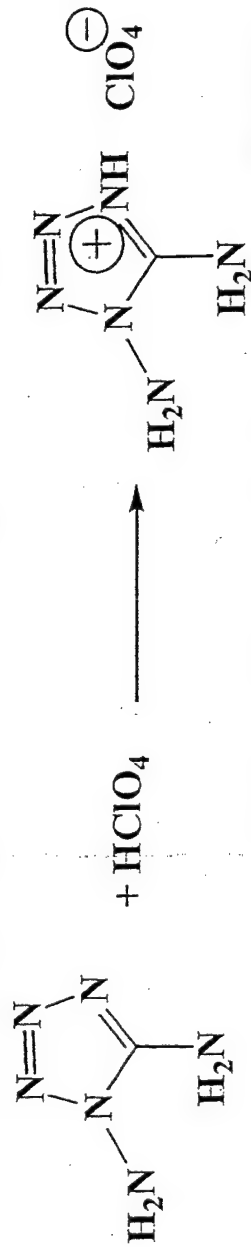
Drake, G.; Hawkins, T.; Boatz, J.; Hall, L.; Brand, A. Prop. Expl. Pyrotech. **2004**, to be submitted  
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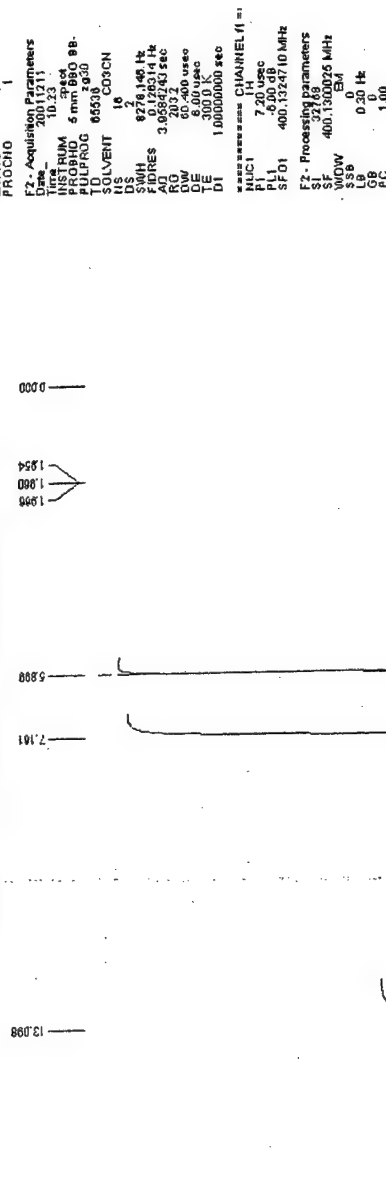
# AFRL Ionic Liquids



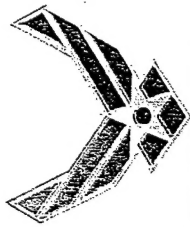
Experimental points to proton going on tetrazole ring, which disagrees from Russian findings



crystals of 1,5-diaminotetrazolium perchlorate in CD<sub>3</sub>CN



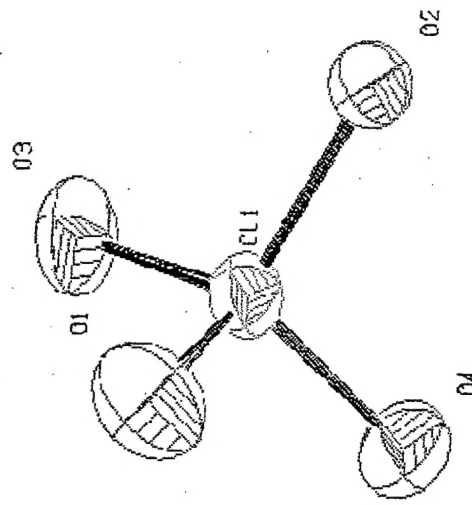
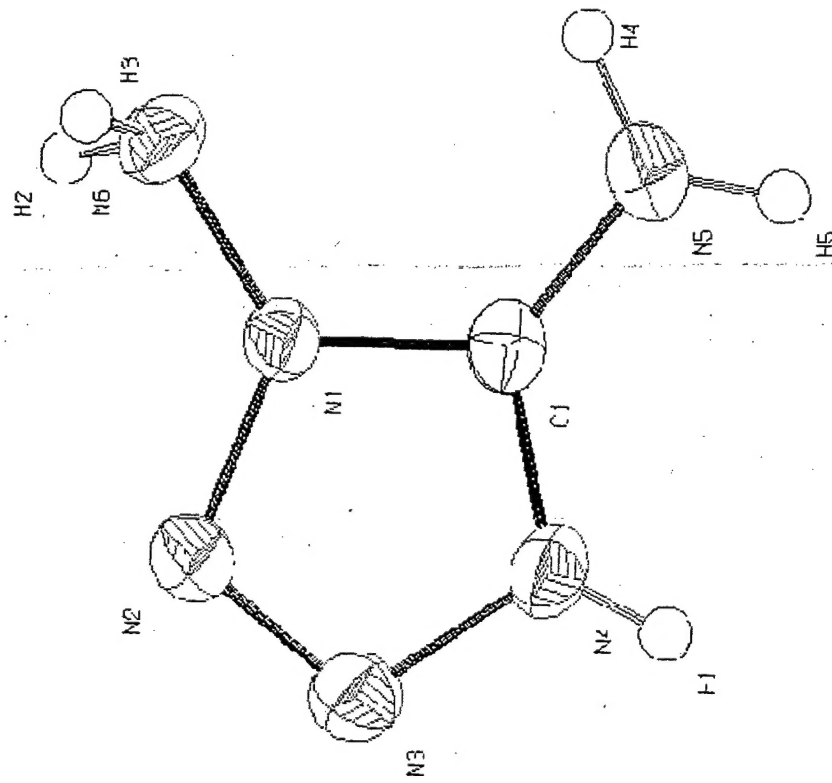




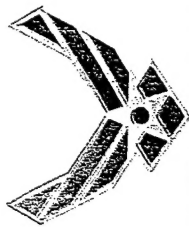
# AFRL Ionic Liquids



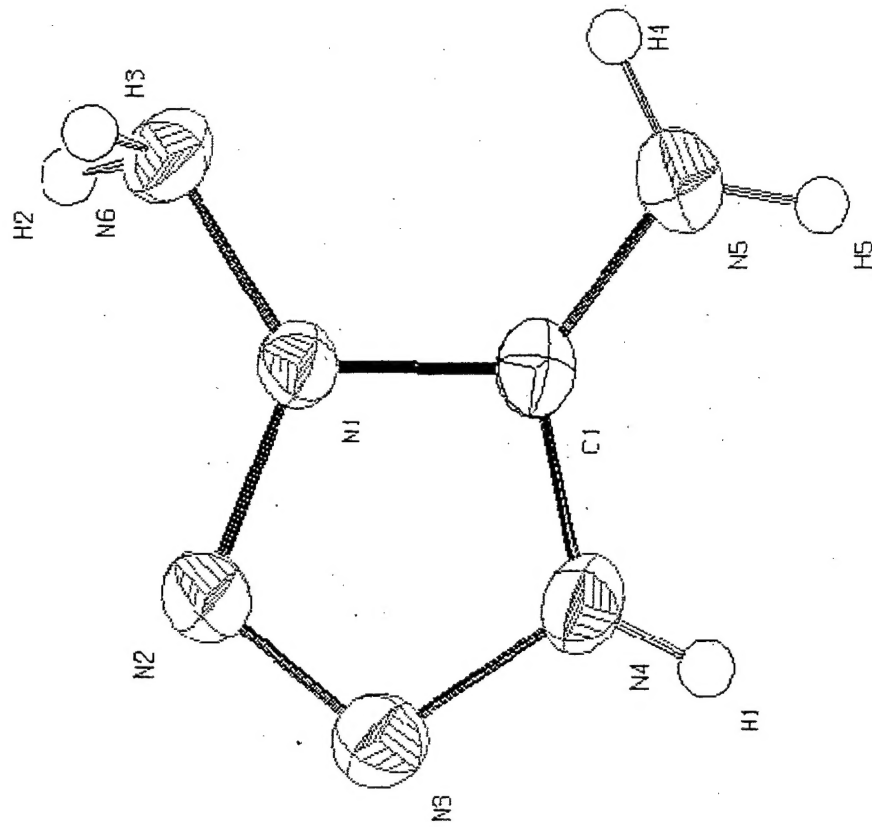
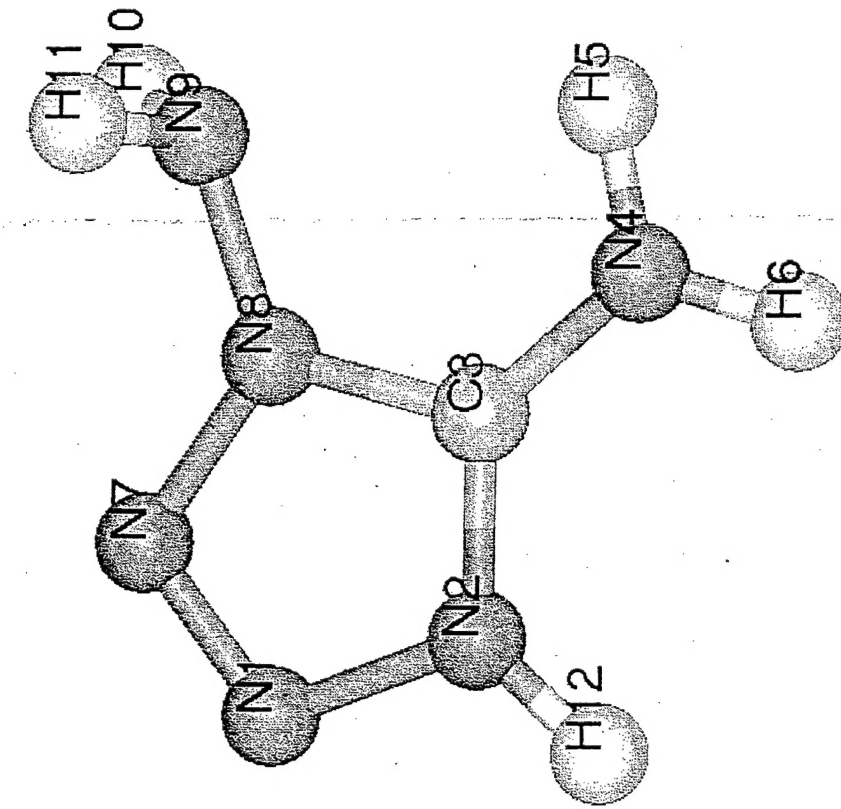
## Single crystal x-ray diffraction study of 1,5-diamino-1,2,3,4-tetrazolium perchlorate



Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. *Prop. Explos. Pyro.* **2004**, Submitted  
Distribution A. Public Release, Distribution unlimited

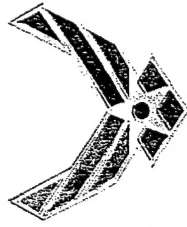


# AFRL Ionic Liquids



Theory and Experimental Structures of 1,5-diamino-1,2,3,4-tetrazolium perchlorate are in close agreement in distances and angles.

Drake, G.; Hawkins, T.; Vij, A.; Hall, L.; Boatz, J. *Prop. Explos. Pyro.* 2004, Submitted  
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# AFRL Ionic Liquids

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## Summary and Conclusions

Hydrogen bonding is highly important in all systems

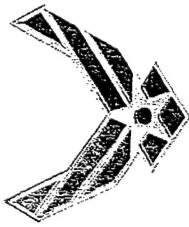
Asymmetry can dramatically affect physical properties and modest changes can have drastic affects.

N-amino heterocycles offer a rich platform for ionic liquids

New triazole and tetrazole systems have been identified as ionic liquid precursors

X-ray crystallography continues to be a powerful tool in identifying interactions in the solid state.

There are a lot of possibilities out there that await development....



# AFRL Ionic Liquids

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